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Preliminary communication

The relevance of the nuclearity of the metal in the cocyclization of α,ω-diynes and nitriles catalyzed by mesitylene solvated cobalt atoms; preliminary EPR studies

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Abstract

The clustering when mesitylene-solvated cobalt atoms are allowed to warm from the cocondensation temperature, affords cobalt compounds of both low and high nuclearity which have different catalytic properties in the synthesis of pyridines from α,ω-dialkynes and nitriles.

Catalysts derived from cobalt atoms have recently been shown to be very active in the synthesis of pyridines from acetylenes and nitriles [1]. The reaction of α,ω-diacetylenes and nitriles was of particular interest, annelation to cycloalkene-pyridines being observed when cobalt vapour was introduced directly into the reagents, and unexpected cyclization to alkynylpyridines when cobalt-arene cocondensates [2] (arene = toluene, mesitylene) were used as catalysts (Scheme 1). In both cases diyne oligomers were also formed as by-products. In order to gain a better insight into these different activities we undertook studies on the nature of the cobalt-mesitylene cocondensates. The products from cobalt vapour and mesitylene, which are stable at low temperature (ca. $-40\,^\circ$C) in mesitylene solution, have been found to give EPR signals. The EPR spectrum at $-35\,^\circ$C shows a group of structured signals centered at $g \simeq 2$, along with very strong broad signals (Fig. 1). The broad part of the spectrum can be related to the presence of high nuclearity cobalt clusters, while the structured signals indicate the presence of lower nuclearity cobalt compounds [3]. For a high nuclearity cluster the number and the spread of the values of the hyperfine interactions can account, at least qualitatively, for many of the various contributions to the lineshape over a very broad range of values. For a small cluster, perhaps having a well defined geometry, a narrower and more

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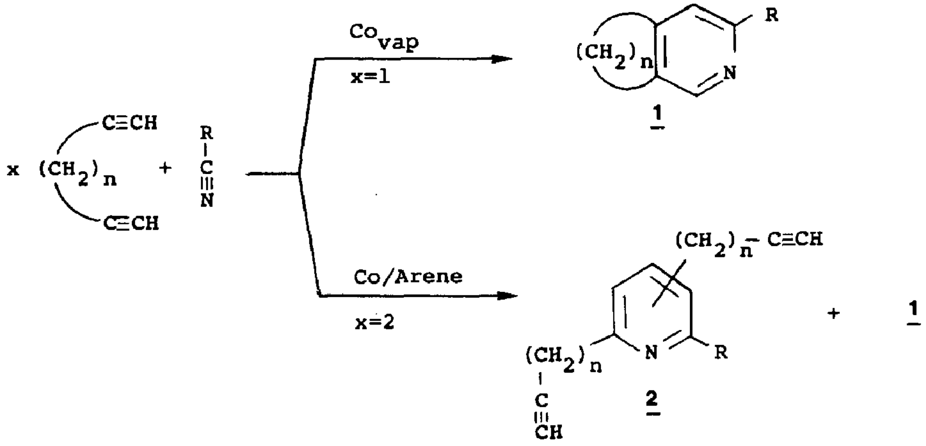

Scheme 1

structured lineshape is to be expected. The changes in the EPR spectrum as temperature is raised have been analysed. At −15 °C the solution turns from brown to red, and a brown solid separates. The EPR spectrum of the red solution (Fig. 2) is similar to the structured part of the spectrum recorded at −35 °C, indicating that the low nuclearity cobalt species are still present whereas the high nuclearity cobalt clusters have grown to give mesitylene-insoluble compounds.

The brown precipitate and the red solution formed from the reaction mixture on standing at −15 °C have been separated, and tested as catalytic precursors for the cyclization of 1,7-octadiyne and acetonitrile. Their catalytic activities have been compared with that of the starting cobalt-mesitylene cocondensation products. The results are summarized in Table 1.

As reported previously [2], the cocyclization of 1,7-octadiyne and acetonitrile catalyzed by cobalt-mesitylene cocondensate (I) affords 3-methyl-5,6,7,8-tetrahydro-

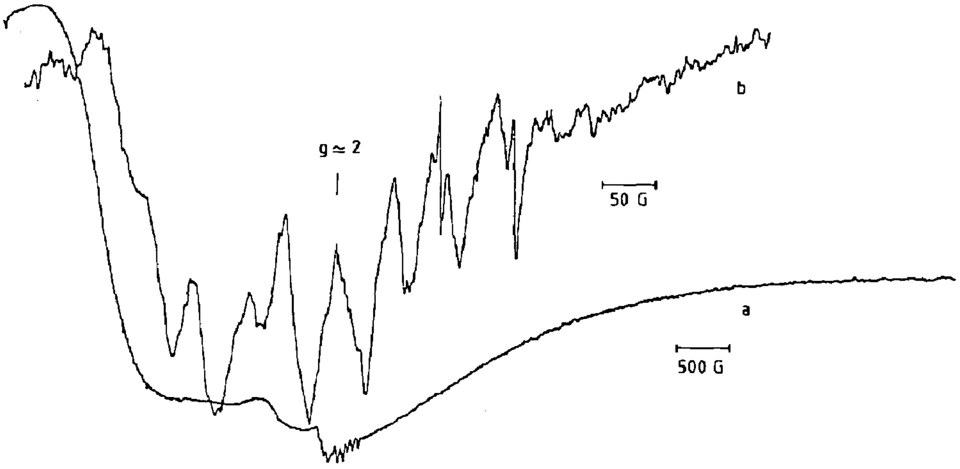

Fig. 1. EPR spectrum of cobalt in mesitylene recorded at −35 °C on an E112 Century Series Varian spectrometer, microwave power = 10 mW and microwave frequency = 9.378 GHz; (a) overall H_0 sweep-width = 10 000 Gauss, (b) overall H_0 sweep-width = 1 000 Gauss showing the structured part of the spectrum a.

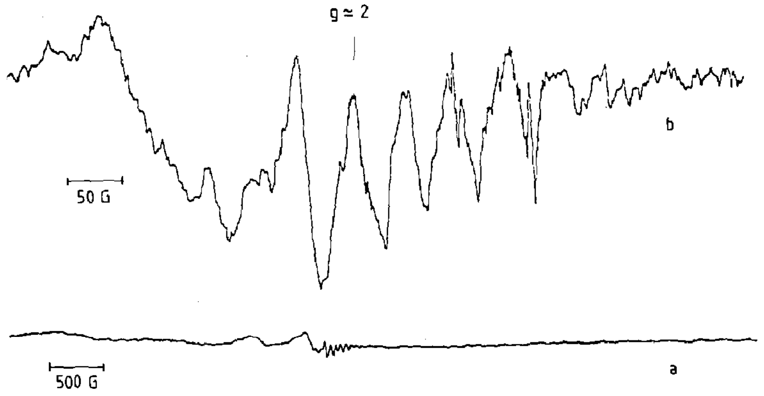

Fig. 2. EPR spectrum of cobalt in mesitylene at −15 ° C, microwave power = 10 mW and microwave frequency = 9.378 GHz; (a) overall H_0 sweep-width = 10 000 Gauss, (b) overall H_0 sweep-width = 1 000 Gauss showing the structured part of the spectrum a.

quinoline, (**1**) and the unexpected dihexynyl-2-methylpyridines, (**2**), to the extents of 45 and 55%, respectively, at room temperature. With the low nuclearity cobalt clusters as catalytic precursors, Ia, obtained from I on standing at −15 ° C, the cocyclization affords almost exclusively the annelated pyridine **1**. In contrast, the brown precipitate Ib, which separates out from I as a result of clustering, catalyzes the formation only of the dialkynyl-2-methylpyridines.

These results reveal the importance of the degree of nuclearity of the metal in the cocyclization of 1,7-octadiyne and CH_3CN catalysed by mesitylene-solvated cobalt atoms. Annelated pyridines are selectively formed when low nuclearity cobalt species Ia are used, whereas the high nuclearity cobalt clusters catalyse the formation of alkynylpyridines.

Since catalysts giving annelated products have been suggested to coordinate with both triple bonds of the diyne [4], the differing behaviour of the cobalt catalysts indicates that the diyne molecule can only act as a bidentate ligand towards mono- or low-nuclearity cobalt catalytic precursors. The selective formation of annelated pyridines when cobalt vapour is directly introduced into the substrates can thus be accounted for by assuming that cobalt, like most metals, vaporizes as monoatomic species, and that clustering to high nuclearity compounds on warming from the

Table 1

Synthesis of pyridines from 1,7-octadiyne and CH_3CN catalyzed by mesitylene-solvated cobalt atoms [a]

Co catalyst [b]	Conversion of dialkyne (%)	Distribution of pyridines (%) [c]	
		1	2 [d]
1	36	45	55 [e]
1a	28	~100	traces
1b	32	traces	~100 [f]

[a] 1,7-Octadiyne 15 mmol; CH_3CN/dialkyne (mol/mol) 5; room temperature; reaction time 48 h; work-up by acid-base separation. [b] 1 = Co-Mesitylene cocondensate isolated at −40 ° C, in mesitylene solution (Co vaporized 50 mg; 0.8 mg-atom); **1a** = red solution derived from **1** on standing at −15 ° C; **1b** = brown precipitate derived from **1** on standing at −15 ° C. [c] As indicated by GLC. [d] As mixture of 4,6- (**2a**), and 3,6-di-5-exynyl-2-methylpyridine (**2b**). [e] **2a**/**2b** molar ratio 4. [f] **2a**/**2b** molar ratio 2.5.

cocondensation temperature is unlikely in the presence of stabilyzing ligands such as diynes and nitriles. The clustering of solvated metal atoms is an important process in metal vapour chemistry; it depends strongly on the temperature used for isolation of the metal-solvent cocondensation products, and this provides a promising tool for the preparation of naked metal clusters of various sizes and particular catalytic activities [5].

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